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INVESTIGATION INTO THE REACTIONS OF ALIPHATIC METHOXYDIAZO -KETONES UPON TREATMENT WITH BORON TRIFLUORIDE ETHERATE

UC
Thesis

by

Donald P. Hoster III UC 1963

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Senior Thesis Submitted
in Partial Fulfillment
of the Requirements for Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

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INVESTIGATION INTO THE REACTIONS OF ALIPHATIC METHOXYDIAZO -KETONES UPON TREATMENT WITH BORON TRIFLUORIDE ETHERATE

By

Donald P. Hoster

A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

By Donald P. Hoster

Approved by Howard E. Shoffer

May 20, 1963

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I would like to express my sincere gratitude to Dr. Howard E. Sheffer of the Union College Chemistry Department for his advice and constant assistance throughout the course of this research project.

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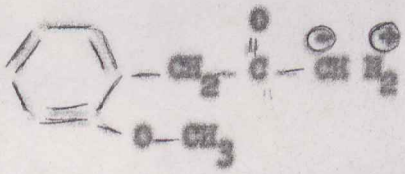
INTRODUCTION

This research was a study of the possible cyclization reactions of the aliphatic methoxydiazoketones (I) and (II) upon treatment with BF_3 etherate. Previous work in this area had dealt with aromatic systems.

(I) $CH_3OCH_2COCHN_2$ (II) $CH_3OCH_2CH_2COCHN_2$

J. Moore and H. Shaffer[10] showed that 1-diazo-3-(o-anisyl)-2-propanone (XII) is converted in about 35% yield to chromanone (IV) upon treatment with BF_3. They obtained lesser amounts of chromanone and larger

(XII)



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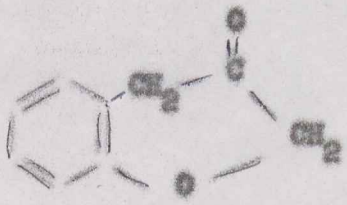
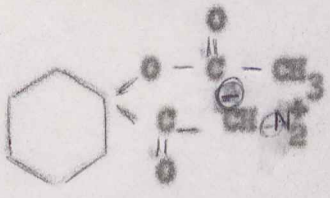


amounts of open chain products when mineral acids were employed. Diazoketones such as (V) and (VI) have shown a pronounced tendency to form four-membered rings upon treatment with mineral acids.[9] No open chain products were isolated in the latter case even in the presence of

(V)



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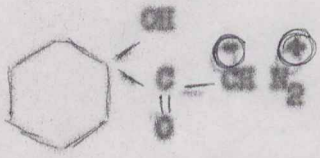
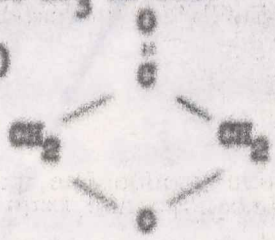
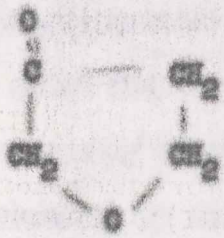


excess nucleophile ($\ddot{X}:$). The formation of five and six-membered rings has generally been limited to the sterically favorable ortho-substituted aromatic forms.

Based on the fact that the Lewis Acid, BF_3, gave the best yield of cyclic product in the aromatic system a similar result might be expected from the aliphatic series. The object of this research was to produce the cyclic compounds oxetanone-3 (VII) and tetrahydro-3-furanone (VIII) by the BF_3 method.

(VII) 

(VIII) 

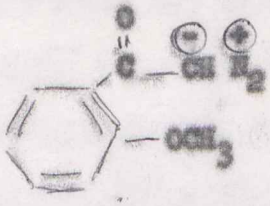
The diazoketones which appear in this paper will be written as $RCOCHN_2$ although the actual structure is a resonance hybrid of the three forms below:

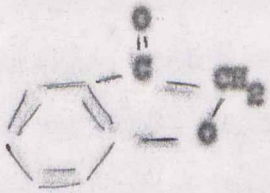
(A) (B) (C)

HISTORICAL

Diazoketones ($RCOCHN_2$) where R is any alkyl or aryl group were discovered at the beginning of this century by the German chemist, L. Wolff[11]. He is best known for his studies which eventually led to the formulation of the Wolff rearrangement, a process whereby diazoketones are transformed into carboxylic acids in the presence of silver ions. F. Arndt and B. Eistert[11] subsequently discovered that carboxylic acid chlorides can be converted to diazoketones by treatment with an excess of a cold ethereal solution of diazomethane.

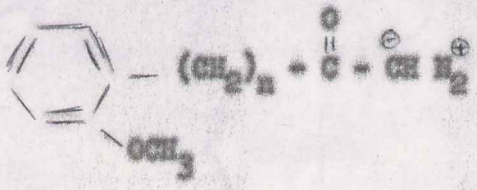
Early workers soon discovered that diazoketones decomposed readily at room temperature by evolving nitrogen gas. They are rapidly decomposed in acid solution to a variety of products of which substituted methyl ketones are predominant. Exceptions were found among the aromatic diazoketones with appropriate ortho substituents which underwent cyclization reactions in the presence of acids. A. K. Bose and P. Yates discovered that α-diazo-o-methoxyacetophenone (IX) is converted to coumaranone (X) in the presence of mineral acids.[2]

(IX) 

(X) 

Elderfield and his co-workers discovered that α-diazo-o-acetylacetophenone when treated with glacial acetic acid also underwent a cyclization reaction to coumaranone (X).[7] Last year Moore and Sheffer extended

this work and concluded that ortho-methoxy aromatic diazoketones of the form below undergo cyclization best when a Lewis Acid such as BF_3 is employed and when (n) is zero or one. However, open chain fluoro,



hydroxy and ethoxy substituted methyl ketones were also isolated from the reaction mixture.(10)

Evidently, no attempts to prepare tetrahydro-3-furanone (VIII) by a diazoketone synthesis have been made to date but an attempt to prepare oxetanone-3 has been carried out by Kennar and Richards as well as by Marshall and Walker.(6,8) Each used a different acid and each reported only insignificant yields of cyclic products.

Kennar and Richards prepared methoxyacetyl chloride from methoxy-acetic acid and dissolved this in anhydrous ether. This was then added to an excess of diazomethane in ether at 0-5° C. After letting the mixture stand for 20 hours and subsequent removal of solvent, 50 ml. of 0.5N H_2SO_4 was added to the yellow residual oil. After the evolution of nitrogen gas had ceased the solution was saturated with sodium acetate and stored for another 20 hours. Finally the mixture was extracted with ether in the presence of barium carbonate and dried over anhydrous calcium sulfate. The ether was distilled off and two fractions were isolated.

The first fraction had a boiling point of 40-85° C at 21mm. This fraction formed a derivative with 2,4-dinitrophenylhydrazine which melted at 205° C upon recrystalisation. Kenner and Richards reported this as the 2,4-dinitrophenylhydrazone of pyruvaldehyde (XI) based upon a mixed melting point determination[6]. However, Heilbron's Dictionary of

(XI) CH_3COCOH

Organic Compounds does not list pyruvaldehyde as forming a 2,4-dinitro phenylhydrazone but rather a bis-2,4-dinitrophenylhydrazone with a melting point of 299-300° C.[5] Consequently the accuracy of the above work is in doubt.

The second fraction had a boiling point of 89-90° C at 21 mm and an index of refraction (n_D^{23} = 1.4367). This compound reduced Fehling's solution and gave a 2,4-dinitrophenylhydrazone which upon recrystalization melted at 175° C. Carbon-hydrogen analysis of the original material and carbon-hydrogen-nitrogen analysis of the derivative showed this compound to be the open-chain hydroxy compound (1-hydroxy-3-methoxy-2 -propanone) (XII). No mention of any other products was made.

(XII) $CH_3OCH_2COCH_2OH$

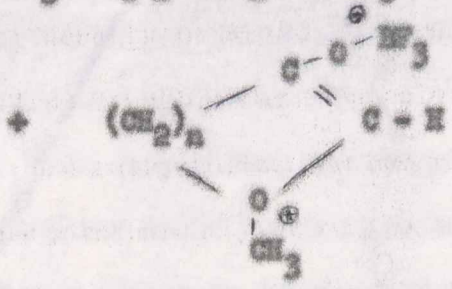
Marshall and Walker prepared chloroacetyl chloride from chloroacetic acid and dissolved this in an excess of diazomethane in ether at 0-5° C. After the nitrogen evolution had ceased the ether was taken off under vacuum and the residual yellow oil was treated with methyl alcohol,

potassium carbonate and water. After standing for four hours the entire mixture was refluxed with glacial acetic acid. Three fractions were isolated but only the first fraction which had a boiling point of 90-118° C at atm. pressure proved interesting. About 3 grams of product were isolated which represented a yield of only a few percent. This first fraction formed a pale orange 2,4-dinitrophenylhydrazone which upon recrystalisation had a melting point of 152-155° C. A carbon-hydrogen analysis of the derivative gave fair agreement with the DNP derivative of Cmetanone-3. No other compounds were isolated.

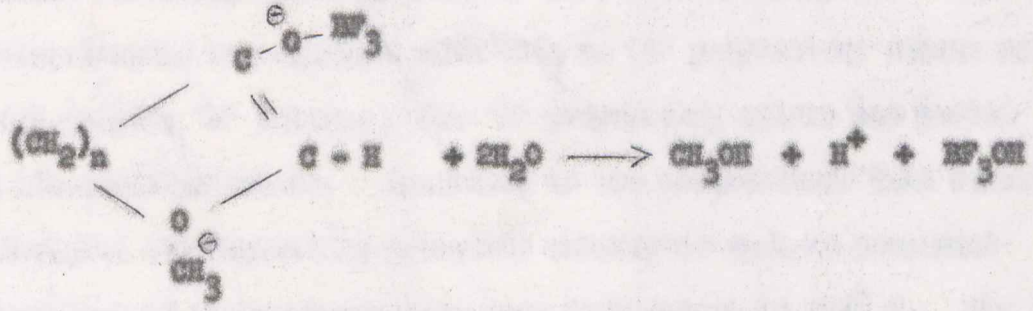
Moore and Sheffer have suggested that since relative nucleophilicity is a controlling factor in bringing about ring-closure in any system, the use of $BF_3 \cdot Et_2O$ should enhance the nucleophilicity of the methoxy-oxygen atom.[10] Obviously competition from the anions of the mineral acids is now eliminated. This mechanism as applied to aliphatic methoxydiacetones is illustrated.

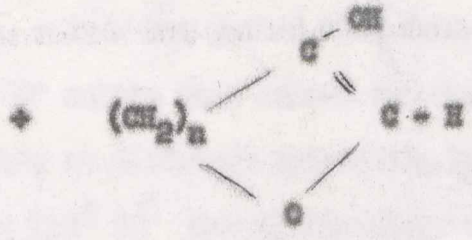
A Proposed Mechanism For Ring Closure Reactions of Aliphatic Methoxydiazoketones Upon Treatment with $BF_3 \cdot (C_2H_5)_2O$

(1) $CH_3O(CH_2)_nC\overset{\ominus}{O}\overset{\oplus}{C}HN_2 + BF_3 \cdot (C_2H_5)_2O \longrightarrow N_2 + (C_2H_5)_2O$

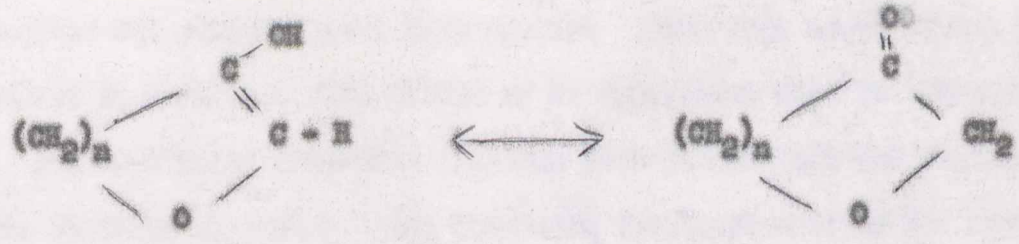


(2)





(3)



APPARATUS

A four ft. X 1/2 in. fractional distillation column was used for stripping the ether from the reaction products in most cases. A small one-piece glass Vigreux column convenient for fractionally distilling quantities of 50 grams or less was used for fractionally distilling the reaction products.

More specialized apparatus was later employed among which the Perkin-Elmer Model 154-D vaporfractometer and the Perkin-Elmer Model-21 infra-red recording spectrophotometer were notable examples. The vaporfractometer was equipped with both an "A" preparatory column and a general purpose "R" column. The "A" preparatory column was packed with diisodecylphthalate. According to the manufacturer this column was designed for separating non-polar substances such as saturated hydrocarbons at temperatures from room temperature to 179° C. The "A" prep. column was packed with Ucon-polyglycol, LB-550-X. In contrast to the "A" column this column was designed for separating quite a wide variety of different materials, both polar and non-polar, at temperatures up to 200° C. The Perkin-Elmer Model-21 infra-red recording spectrophotometer was equipped with NaCl optics. Materials could be run pure or dissolved in a solvent with little or no absorbance such as chloroform.

The vaporfractometer was employed both in analysis and separation of the reaction products. The infra-red spectrophotometer was useful in determining the functional groups present in the various reaction products.

The rest of the apparatus consisted of the usual laboratory equipment. However, at one point a concentric tube fractionating column with 75 theoretical plates equipped with a solenoid for variable reflux rate was employed.

EXPERIMENTAL

Preparation of β-Methoxypropionic Acid:

β-Methoxypropionic acid for use in the synthesis of 1-diazo-4-methoxy-2-butanone was prepared by the method proposed by Christian and Hixon.(3) Five moles of β-methoxypropionitrile (Eastman Kodak) and 10 moles of concentrated HCl were heated and stirred for two and a half hours with a mechanical stirrer at a temperature of 70-80° C and finally for the last half hour at 100° C. The organic products were extracted with ether and the ether removed under water-pump vacuum. The residue was vacuum-distilled and two major fractions, the first boiling at 35-92° C at 20 mm. and the second boiling at 115-120° C at 17-22 mm., were isolated. The first fraction was determined to be unreacted nitrile and the second was determined to be the acid from boiling point references.(1) A yield of 19% (99g.) of acid was obtained. The purity was found to be 90% by neutralisation equivalent.

Preparation of Methoxyacetyl Chloride:

Methoxyacetyl chloride was prepared from methoxyacetic acid (Kodak) b.p. 203-205° C by the method of Fieser.(4) The acid (1.67 moles) was reacted with 1.67 moles of thionyl chloride b.p. 77° C. A yield of 72% of methoxyacetyl chloride boiling at 106-109° C was obtained. The addition of a 50% excess of thionyl chloride was found to be inadvisable in this case due to the serious problems of separation

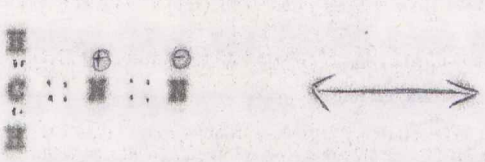
by distillation which resulted. The methoxyacetyl chloride was used in the preparation of 1-diazo-3-methoxy-2-propanone. The acid chloride was redistilled before use to increase its purity.

Preparation of β-Methoxy Propionyl Chloride:

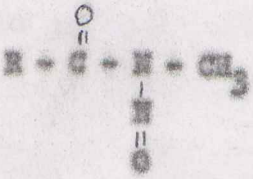
β-methoxypropionyl chloride was prepared from β-methoxy-propionic acid. The acid (0.95) moles and 0.95 moles of thionyl chloride were reacted in the conventional manner and 87.1 g. (75% yield) of β-methoxy-propionyl chloride b.p. 136-138° C were isolated. The β-methoxypropionyl chloride was redistilled before using it to prepare 1-diazo-4-methoxy-2-butanone in order to increase its purity.

Preparation of Diazomethane for Use in Preparing Diazoketones:

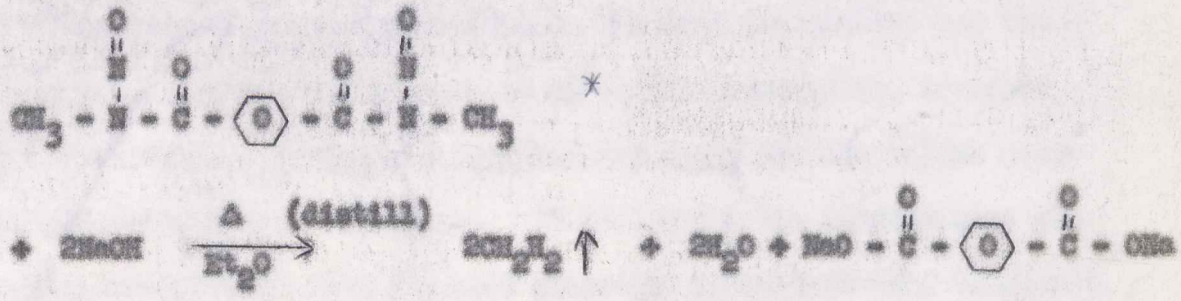
Diazomethane is a toxic yellow gas very soluble in ether and heavier than air. The structure is a resonance hybrid of the two forms:

(A)  (B) 

Diazomethane is released when alkali acts on any N-methyl, N-nitroso group such as:



The diazomethane prepared for use in carrying on this research project was prepared by the method of Reed and Moore.[9] The diazomethane precursor and NaOH were reacted according to the following equation:



(N,N' - dimethyldinitroso terephthalamide)
(E.I. DUPONT CO.)

Two 5 liter flasks were employed for this preparation, one for distilling and one for receiving. The two flasks were connected by adapters and a 60 cm. long condenser. The receiving flask was packed with an ice-salt bath to reduce the danger of an explosion. Needless to say, the entire operation was carried out in a well-ventilated hood. An electric heating mantel was used for heating the reaction mixture. The receiving flask was filled each time with enough ether to cover the tip of the adapter in the receiving flask. This was done in order to insure a minimum loss of diazomethane from the receiving flask. Each batch was planned for a theoretical yield of CH_2N_2 of 1 mole. The actual amount usually obtained was about 0.8 mole and was checked by reaction with benzoic acid and back titration with sodium hydroxide in the first preparation. This amount of diazomethane was sufficient for each reaction with 0.2-0.4 mole of acid chloride since at least a 2:1 excess of diazomethane is necessary.

Three liters of ether, 450 ml. of diethyleneglycol-monoethyl ether (Matheson, Coleman and Bell) and 600 ml. of 30% NaOH were thoroughly mixed and brought to a temperature of 5° C. At this point 180 g. of the diazomethane precursor was added to the reaction mixture and the mixture heated on the heating mantel until the diazomethane in ether began to distill. It usually required 2-3 hours for the yellow color of the diazomethane to disappear. At this point the diazomethane was suitable for reaction with the acid chlorides without further treatment.

Preparation and Reaction of 1-Diazo-3-Methoxy-2-Propanone:
(First and Second Attempts)

Methoxyacetyl chloride (0.2 moles) in 100 ml. of anhydrous ether was added to a freshly prepared batch of diazomethane at 5° C. The addition was accompanied by vigorous nitrogen evolution. This mixture was set outdoors in the sunlight for two days and the polymerized material removed by filtration at the end of the period. The remainder was evaporated under water pump vacuum and heat to remove the ether. Due to the large amount of polymeric material which had formed and the deep red color of the diazoketone it was decided to abandon any further studies on this batch.

The process was repeated with another 0.2 mole of methoxyacetyl chloride except that the reaction mixture was not allowed to stand in the sun and no heat was used while evaporating the ether under vacuum. The diazoketone was treated with 0.2 mole (28.4g.) of the BF_3-ether

complex dissolved in 450 ml. of anhydrous ether. This process was accompanied by vigorous nitrogen evolution. After an hour or so the reaction mixture was transferred to a 2 l. separatory funnel and extracted with three 50 ml. portions of distilled water and one 50 ml. portion of 10% $NaHCO_3$ to remove the BF_3 complexes. The ether was then evaporated under water pump vacuum and the remainder fractionally distilled in a small vigreux column.

Five fractions were isolated, the first containing 5.7 g. and boiling 36-45° C, the second containing 1.8 g. and boiling 45-96° C, the third containing 0.8 g. and boiling 96-101° C, the fourth containing 3.6 g. and boiling 71-82° C at 26 mm and the fifth containing 0.5 g. and boiling 76-124° C at about 20 mm. The second and fourth fractions were checked on the Perkin-Elmer Model 154-D vaporfractometer using the "R" column. The second fraction showed two major peaks of about equal height and retention time. The first peak was shown to be ether by peak enhancement. The fourth fraction showed two major peaks and three minor peaks. The first major peak was shown to be ether by peak enhancement. Since the quantities involved were so small, it was evident that further separation by fractional distillation was out of the question. The second fraction gave a weakly positive test for the carbonyl group with $NH_2OH \cdot HCl$ reagent while the fourth fraction gave a very strong positive test with this reagent. The fourth fraction also showed evidence of the (OH) group from its reaction with cerric nitrate reagent while fraction two was negative for (OH) with this reagent.

The second fraction did not give a derivative with 2,4-dinitrophenylhydrazine and only the reagent itself could be recovered. Fraction No. 4 afforded only a very small amount of derivative (3-4% yield) which melted at 290-295° C (uncorrected). This derivative was deep orange in color and was not soluble in boiling ethanol or dioxane.

Preparation and Reaction of 1-Diazo-3-Methoxy-2-Propanone:

(Third Attempt)

This batch was run with the intent of using 0.4 moles of acid chloride instead of 0.2 moles in order to obtain a larger amount of crude product. However, upon checking the concentration of the CH_2N_2 in the solution it was found that a 2:1 excess of CH_2N_2 would not be insured if this were done. Consequently this plan was abandoned and only 0.2 mole of methoxyacetyl chloride was added. If sufficient CH_2N_2 is not present, the HCl which is released upon addition of the acid chloride will react with the diazoketone to give chloromethyl ketone.

The reaction sequence was similar to the previous attempts except that the ether was separated from the final products by employing a 4' X 1/2" column packed with stainless steel helicies to improve the separation of any cyclic (low-boiler) from the ether. Moreover, the ethereal solution of products was dried over anhydrous sodium sulfate to remove any water that might be present.

The material which remained after the ether was removed was fractionally distilled in a vigreux column. Two fractions were isolated this time, the first boiling at 58-62° C at 12-15 mm containing 5.0 g. and the second at 89-105° C at 13 mm containing 0.4 g. Polymeric residue (1.65 g.) was also obtained. The boiling point of the first fraction seemed to indicate the presence of the open chain hydroxy-compound (1-hydroxy-3-methoxy-2-propanone).(6) If this fraction contained nothing but pure ketal the yield would be about 25%. Fraction No. 1 formed a 2,4-dinitrophenylhydrazone (14% yield) which contained at least three different types of crystals: (1)-Needles-90° C (2)-Orange Plates-175-185° C (3)-Red Granules-195-205° C. The orange plates corresponded roughly to the 2,4-DNP of 1-hydroxy-3-methoxy-2-pro-panone as reported by Emmer and Richards.(6) Fraction No. 2 did not form a derivative with 2,4-dinitrophenylhydrazine. Fraction No. 1 was analyzed by gas chromatography and showed three major peaks and three minor peaks. The first of the major peaks was shown to be ether by peak enhancement. The second peak did not correspond in any way to any of the peaks obtained in previous analyses. The third peak, however, did correspond to the second peak obtained from fraction No. 4 of the previous run, retention time being the criterion employed.

Preparation of 1-Diazo-4-Methoxy-2-Butanone:

β-methoxypropionyl chloride (0.35 moles) was added to a batch of diazomethane. This was followed by a vigorous evolution of nitrogen

gas. The nitrogen was collected over water and the amount collected indicated a 93% yield of the intermediate diazoketone. The reaction mixture was worked up in the conventional manner and the ether stripped off on the 4' x 1/2" fractional distillation column. The reaction mixture was fractionally distilled in a vigreux column as in the previous runs. The first fraction contained 9.4 g. and boiled at 35-40° C. The second fraction boiled at 135-152° C and contained 0.9 g. The third fraction boiled at 58-72° C at 12 mm and contained 1.3 g. The fourth fraction boiled at 96-124° C at 12 mm and contained 6.7 g. None of these fractions would form 2,4-dinitrophenylhydrazones. These fractions were not analyzed by gas chromatography and further work was discontinued in order to concentrate on the reaction of 1-diazo-3-methoxy-2-propanone in the hope of obtaining some definite results.

Preparation of Methoxyacetyl Chloride:

(Second Batch)

More methoxyacetyl chloride for use in preparing 1-diazo-3-methoxy-2-propanone was made by the method discussed on page 11. The acid chloride boiled at 106-109° C and 173 g. (1.6 moles) of product were isolated representing a yield of 80%.

Preparation and Reaction of 1-Diazo-3-Methoxy-2-Propanone:

(Fourth Attempt)

Four batches of diazoethane in ether were treated with four portions of 0.4 mole methoxyacetyl chloride. The reaction mixtures were each worked up by treating with boron trifluoride-etherate and extracting the BF_3 with three 50 ml. portions of distilled water and one 50 ml. portion of 10% aqueous sodium bicarbonate. The ether was stripped off on a four foot column and the residue dried with anhydrous sodium sulfate. This material was then fractionally distilled in a small vigreux column as in previous attempts. The following results were obtained upon fractionation:'

TABLE A

Fraction Number	Boiling Range	Pressure	Weight
1	52-70° C	Atm.	5.32 g.*
2	70-78° C	"	4.92 g.
3	78-86° C	"	7.11 g.
4	41-50° C	15-20 mm.	4.39 g.
5	60-116° C	16-20 mm.	21.47 g.
6	residue	------	29.21 g.

* Azeotrope consisting of two layers.

The above material was checked out on the 154-vaporfractometer using the "R" column and found to be quite impure. Since more material was available than on previous attempts, a redistillation was deemed advisable. The results of this refractionation are listed in Table B as well as pertinent infra-red and vapor-phase data

TABLE B

Fraction Number	Boiling Range	Pressure	Weight	Number of Major Vapor Phase Peaks	Infra-Red Absorbances
1	42-53° C	Atm.	0.3 g.	5	-----
2	54-58° C	Atm.	1.7 g.	5	-OH, R-O-R -C=O, Alkyl
3	59-61° C	Atm.	1.9 g.	5	-----
4 & 6	62-70° C	Atm.	0.9 g.	3	-OH,-C=O,ROR Alkyl
5 & 7	73-77° C	Atm.	3.2 g.	3	-----
8	77-84° C	Atm.	3.0 g.	2	-----
9	86-94° C	Atm.	0.9 g.	2	-OH,-C=O,-C-? R-O-R,Alkyl
10	48-62° C	45 mm.	1.8 g.	2	-----
11	62-66° C	45 mm.	4.8 g.	4	-----
12	43-46° C	2-3 mm.	0.1 g.	-	-----
13	72-74° C	1-2 mm.	0.85 g.	-	-----
14	74-88° C	1 mm.	7.9 g.	3	-OH,-C=O,-C-? R-O-R, Alkyl
15	106-124° C	1 mm.	5.8 g.	3	Same

The above data seemed to indicate that each fraction was still very impure. At this point it was decided to attempt separation by gas chromatography using the "A" preparation column instead of trying another fractional distillation in the vigreux column.

Attempted Separation by Gas Chromatography:

Fraction No. 8 in Table B was chosen for the attempted separation by this method since it appeared to contain only two constituents by a preliminary vapor-phase analysis on the "B" column. This fraction as well as fractions 9 - 15 was found to be free of ether. Fractions 1 - 7 were found to contain ether on the basis of peak enhancement and retention time.

The Perkin-Elmer Model-154-D vaporfractometer was fitted with the "A" prep. column and various size samples and column temperatures were tried. It was discovered that maximum separation occurred when a sample of approximately 0.5-1.0 cc. was introduced at a column temperature of 60° C. Even under these conditions there was considerable overlapping of the two peaks. Thus complete separation by this method using the "A" column appeared to be impossible. Fraction No. 8 from Table B was separated into two semi-pure parts by condensation of the effluent vapor in a dry-ice acetone bath. The recovery of starting product under these conditions was about 75%.

The two fractions which were isolated by this method were then examined on the same instrument using the "B" column. Upon examination of the results it appeared that the two peaks had switched retention times between the use of the "A" column and the "B" column. Peak No. 2 on the "B" column corresponded to peak No. 1 on the "A" column and vice-versa. Originally, it was planned to make derivatives of these two fractions but this idea was abandoned in favor of saving these

fractions for future possible NMR investigations in spite of the fact that the purity of the samples was hardly adequate. It was also hoped that an "H" prep. column might be used for more efficient separation at a later date.

At this point, it was decided to attempt to make 2,4-dinitrophenylhydrazones out of each of the fractions listed in Table B. Fractions 1, 2, 3, 4 and 6, 12, 13, 14 and 15 did not form any derivative and only the reagent would be isolated upon standing and cooling. Fractions 5 and 7, 8, 9, 10 and 11 afforded a few milligrams of derivative (5% or less) which had an uncorrected melting point of 300° C. This material was not soluble in boiling ethanol or dioxane. The uncorrected melting point corresponds very well with the bis-2,4-dinitrophenylhydrazone of pyruvaldehyde which was reported as a reaction product by Kenner and Richards.(6)

DISCUSSION AND SUMMARY

The synthesis of cantanone-3 and tetrahydro-furanone-3 by the reaction of the corresponding methoxydiazoketones with $BF_3 \cdot Et_2O$ was unsuccessful. Fairly conclusive evidence for the open-chain hydroxy compound (1-hydroxy-3-methoxy-2-propanone) in low yield was obtained. The boiling range of fraction No. 4 (page 15) and fraction No. 1 (page 17) and the 2,4-dinitrophenylhydrazone formed by fraction No. 1 (page 17) agree quite well with the values reported by Kenner and Richards for this compound.(6) Some evidence for the fluoroketone was found in fractions 9 and 14 in Table 2 from the infra-red absorbances at 9.64 μ. No significant evidence for the ethoxyketone was obtained. The 2,4-dinitrophenylhydrazones formed by fraction No. 4 (page 15) and fractions 5 and 7, 8, 9, 10 and 11 (page 20) correspond in melting point to the bis-2,4-dinitrophenylhydrazone for pyruvaldehyde listed in Heilbron.(5) The apparent lack of correspondence between the products and their derivatives isolated from the different runs makes any conclusion as to the products formed in the reaction almost valueless.

It is not too surprising that overwhelming evidence for the cyclics is missing since when the complex on page 8 is hydrolyzed; there exists a 2:1 possibility that the open-chain alcohol will be formed in preference to the cyclic on a purely statistical basis alone. Furthermore, the favorable steric factors resulting from the forced coplanarity of the ortho-substituted aromatic systems due to resonance effects are no longer present.

The separation of the various reaction products with the equipment accessible to us proved to be the most difficult part of the entire project. An "F" prep. column might have enabled us to separate the fractions completely and thus enabled us to obtain positive identifications. A more efficient fractionating column such as a spinning-band type might also have produced material of a higher degree of purity. Column or elution chromatography might also have been employed successfully here. If more time were available, one or all of these techniques would have been employed.

For future work it is suggested that these reactions be carried out using anhydrous (gaseous) BF_3 instead of the ether complex. This would eliminate the ethoxy compound from the possible reaction products and hopefully make the task of separation much easier. It is also suggested that these reactions be tried using substituents other than methoxy groups such as acetyl, hydroxy or nitro groups.

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